Validation of SAGE-III Measurements of NO_3: Ground-Based Vertical Profile Measurements

Status Report for the EOS Validation Program
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Goals of the Investigation

The SAGE III Science Team has established requirements for validation studies to assess the precision and accuracy of the SAGE III measurements of O_3, NO_2, H_2O, NO_3, OClO and other trace species. The work described in this report is aimed at providing ground-based vertical profile and column measurements of NO_3 and NO_2 using the same methodology as the actual SAGE III technique, i.e. lunar and solar occultation in the UV/visible spectral region. Spectra are recorded using two different instruments: a 0.05 cm^{-1} interferometer (FTUVS) and a grating spectrograph, which utilizes a diode, array detector. Both instruments are located at the Table Mountain Facility of the Jet Propulsion Laboratory. Measurements are compared with results from the Caltech/JPL 1-d model to validate mechanisms of stratospheric NO_x chemistry.

Background

Interest in measurements of NO_3 stems from its role as a radical intermediate in the nighttime conversion of NO_x to NO_y. NO_3 is formed primarily in the reaction

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

and removed by the reaction

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M.$$

The significance of this sequence lies in the fact that N_2O_5 is the anhydride of nitric acid, HNO_3, which is an important temporary reservoir of NO_x in the lower stratosphere. The conversion of N_2O_5 to HNO_3 in the stratosphere occurs on the surface of stratospheric sulfate aerosol (SSA) with high efficiency. The rate-limiting process in the conversion of NO_x to HNO_3 through these reactions is the $NO_2 + O_3$ reaction when the SSA surface area is elevated above background conditions. Under background conditions, or at altitudes that lie above the peak in the SSA vertical profile, the conversion rate is limited by the available aerosol surface area. Simultaneous measurements of NO_2, NO_3 and aerosol surface area are therefore key parameters in the understanding of the NO_x budget. Since NO_x plays an important role in the catalytic destruction of O_3 in the lower stratosphere, these measurements are crucial to the understanding of long-term trends in O_3.

Rapid photochemical destruction of NO_3 results in daytime mixing ratios that are extremely small. After sunset, however, this loss mechanism disappears causing NO_3 mixing ratios to increase rapidly. Lunar occultation is therefore an excellent method for the measurement of NO_3 using the technique of long-path visible absorption spectroscopy. While this technique has not yet been used from a satellite platform, it has been employed successfully from balloon and ground-based sensors. The method takes advantage of the intense NO_3 (0,0) absorption band at 662 nm and another strong feature at 623 nm. The spectrum of NO_3 in this spectral region is well established from laboratory studies down to temperatures around 220 K. The spectroscopic determination of NO_3 is affected by interferences from the O_2 $b\,^1\Sigma_g^+(v'=2) \leftarrow X\,^3\Sigma_g^-(v''=0)$ band at 625 nm and a moderately strong water vapor band in the 640-665 nm spectral region. Despite its large cross sections at band peaks, the absorption features of NO_3 are quite weak with slant optical depths ranging from 0.01% to about 1% through the nighttime viewing period.

Methodology

With support from the EOS Validation Program, we have developed a measurement capability for NO_3 to provide correlative measurements for SAGE III and other future spaceborne UV-visible sensors including SCIAMACHY. The approach involves the use of a high resolution (0.05 cm^{-1}) Fourier Transform spectrometer (FTUVS) and a medium resolution grating spectrograph which incorporates a 1024-channel diode array detector. Both instruments operate in the UV-visible-NIR spectral region (0.29-1.1 μm). The FTUVS instrument is based on a plane-mirror Michelson design. The mirror drive is a parallelogram flexure mechanism driven by a voice coil actuator with a stroke of 5 cm. The fixed mirror is actively tilted to maintain alignment within 10% of an interference fringe at 300 nm over the entire stroke. The detector is a single-element silicon avalanche photodiode with a maximum gain of 300. Instrument control, data acquisition and spectral processing are accomplished using parallelized transputers. The grating spectrograph is a commercial 0.3 m Czerny-Turner instrument manufactured by Acton, Inc. The detector for the spectrograph is a commercial Reticon module cooled to –20° C. For applications involving relatively dim sources such as the Moon, the Reticon is superior to a charge-coupled device (CCD) detector due to its much larger well depth. The foreoptics for both instruments consists of a 32-in. dia. heliostat feeding an 8-in. off-axis telescope with f/3 optics. The telescope has dual collimating mirrors, one feeding the spectrometers and the other providing an image to a tracking camera for fine guidance of the heliostat. This capability permits the spectrometers to be pointed at specific features on the solar and lunar disks, which is useful in a number of applications.

Accomplishments

Instrument Improvements

In the past year, several improvements were made to the spectrograph and associated foreoptics to improve the signal-to-noise ratio. The existing Princeton Applied Research Corp. (PARC) 1412 diode array detector head and electronics on the spectrograph were replaced with a Princeton Instruments PDA-1024 diode array detector. The advantages of the new detector include lower operating temperature, higher A/D resolution, lower mass and volume, less etalon channeling and improved software. The spectra obtained using the new detector show less noise and less pixel-to-pixel variability than those obtained using the old detector.

Another significant instrument improvement resulted from refurbishment of the telescope. The telescope, which has been used at TMF since 1994, required recoating of the mirrors and realignment. This was accomplished over a four-month period beginning in September 1999. The telescope was placed back in service in January 2000. A throughput improvement of nearly a factor of two was obtained after the refurbishment.

Algorithm Development

As discussed in the previous report, processing of lunar spectra to obtain the NO_3 column abundance consists of several steps including dark noise subtraction, wavelength calibration using line spectra from a neon emission lamp, ratioing of the spectra with a reference spectrum taken before appreciable buildup of NO_3, and fitting of the resulting absorption spectra using reference spectra for NO_3 and other species including H_2O, O_2, O_3, etc. In the past year, progress has continued on the development of an automated retrieval procedure that follows the above steps. The present approach utilizes the conjugate gradient method to obtain the simultaneous best fit that includes the contributing reference spectra, and a 2nd-order polynomial to account for residual baseline variations.

In order to validate the basic approach, we have begun a program of intercomparisons between our code and the one developed by George Mount (Washington State University) and co-workers at the NOAA Aeronomy Laboratory. The code developed by the NOAA group uses the singular value decomposition method with simultaneous shift and stretch to align the observed spectrum with the contributing reference spectra. The primary goal of the intercomparison is to determine which algorithm results in spectral fits with the smallest overall residuals, and to assess the sensitivity of the derived NO_3 column abundances to the different algorithms. To date we have intercompared spectra acquired on August 25, 1999. The NO_3 column abundances between the two methods agree to within 20%. Further intercomparisons will be carried out in the coming year.

Measurements of NO_3

With the current approach, NO_3 spectra are obtained using the Moon as a light source when the lunar phase is within two days of full. This requirement arises both from the sharp dependence of lunar intensity on lunar phase, and from the need to match the temporal dependence of NO_3 with the availability of the Moon as a target. The number of viewing opportunities is further limited by clouds. Since the last progress report (June 1999), good lunar spectra were obtained on the following 26 days:

6/26/99	9/99: telescope/tracker optics refurbishment begun	4/19/00
6/27/99	1/20/00	4/20/00
6/28/99	1/21/00	
6/29/99	1/22/00	5/17/00
	2/00: new detector installed	5/18/00
7/26/99	2/18/00	5/19/00
7/27/99	2/19/00	
7/28/99	2/20/00	
7/29/99		
	3/18/00	
8/25/99	3/19/00	
8/26/99	3/20/00	
8/27/99	3/21/00	

NO_3 measurements begin at sunset when the column abundance increases from the very low daytime levels, and continue throughout the night. The measurements thus capture the full nighttime cycle of NO_3 formation and destruction as described above. Example NO_3 data sets for the months of March and April 2000 are shown in Figure 1. Significant day-to-day variability is seen in the NO_3 diurnal profiles (factor of 2-3). This is attributable to NO_3 in the troposphere. The large short-term variability in the measured NO_3 columns values (for example at 0730 UTC on 4/19/00) is also indicative of a tropospheric source, perhaps associated with pollution from the Los Angeles urban area. This possibility will be tested once the instrument becomes movable and measurements are made from more pristine sites. Progress toward this objective is discussed in the next section.

Measurement precision is estimated to be ± 5%. Absolute accuracy is estimated to be ± 25%, limited mainly by uncertainties in the spectral fits as revealed by the algorithm intercomparison, and uncertainties in the laboratory cross sections.

NO_3 Measurements Using Stellar/Planetary Objects

As discussed above, NO_3 measurements are currently restricted to a narrow range of lunar phase angles. This will have the effect of limiting the number of validation opportunities for SAGE III overpasses. We have been examining the feasibility of using bright stars and planets as alternate targets for NO_3 measurements. While these objects would offer the possibility of obtaining more measurement opportunities for NO_3, a telescope would be required with an aperture that is larger than the one currently being employed.

In order to assess the feasibility of this approach, tests will be carried out on the Table Mtn. 0.6-m telescope in June 2000. Since this telescope has an f/38 Coudé focus available, it will be straightforward to interface the existing spectrograph/detector to the telescope. Spectra will be recorded using several different celestial objects over a range of object brightnesses and sky positions. The spectra will be analyzed using the existing software to determine how the retrieval precision varies with the measurement parameters. It will then be possible to extrapolate these results to telescopes with other larger or smaller apertures.

Another objective of this study is to determine the best method for the construction of a portable UV/visible spectrometer. The motivation here is to provide a capability for making measurements in locations where the water vapor interference is reduced. As discussed in a previous progress report, there is a water vapor band, which overlaps the 662 nm NO_3 band. Complete removal of the water vapor feature is difficult because several lines in the water vapor band are saturated. A nearby facility that would be nearly ideal for these measurements is Barcroft Observatory in the White Mountain range of California, east of the Sierra Nevada Mountains. At an elevation of over 12,000 ft. and located in the rain shadow of the Sierra Nevada range, Mt. Barcroft is one of the driest places in the world for observational astronomy. The facility at Mt. Barcroft has the infrastructure that would be required to support these measurements. Analysis is underway to determine the requirements for the telescope/pointing system. The results from the tests with the 0.6-m telescope will be very useful in determining these requirements. With this information in hand, design and construction of the telescope will begin with the support provided by the EOS Validation Program.

<u>Planned Activities-FY01</u>

1. The present NO_3 measurement program which uses the 32 in. heliostat and f/3 telescope will continue with spectra being collected at every full Moon opportunity, weather permitting.
2. Work will continue on development of the NO_3 retrieval algorithm. The algorithm intercomparison effort with G. Mount (Washington State University) that began in FY00 will

continue with the goal of identifying possible inadequacies in the spectral fitting method(s) and reference spectra employed.

3. Work will begin on the evaluation of the feasibility of using celestial objects other than the Moon as light sources for the NO_3 measurements. These tests will be carried out on the TMF 0.6-m telescope as determined by the availability of the telescope and group personnel.
4. Results of the tests carried out in (3) will be used in the design and construction of a portable measurement system that can be used at locations other than Table Mountain. The new system will be capable of using the Moon and possibly other celestial objects as nighttime light sources for the NO_3 measurements.

Schedule

Tasks are referenced to the numerical levels in the previous paragraphs

Task/ Month	***Oct 00***	***Nov 00***	***Dec 00***	***Jan 01***	***Feb 01***	***Mar 01***	***Apr 01***	***May 01***	***Jun 01***	***July 01***	***Aug 01***	***Sep 01***
1												
2												
3												
4												

Collaboration with the SAGE III Instrument Team:
There are several areas of mutual interest between our group and the SAGE III Instrument Team including:

- comparison of retrieval algorithms for NO_3 and other species using lunar spectra
- treatment of interfering spectral features
- use of a common spectroscopic database for NO_3 and other molecules
- methods for the comparison of SAGE III vertical profiles with the column and profile data obtained from ground-based sensors
- separation of the NO_3 contributions from the stratosphere and troposphere, especially where regional NO_x sources are important

The PI of this task attended the SAGE III Science Team meeting at Hampton University in February 2000 and the planning meeting for EOS Validation at Snowmass in August 1999. A poster was presented at the Snowmass meeting that described the NO_3 measurements.

Coordination of Table Mountain NO_3 Measurements with SAGE III Overpasses

Since validation of SAGE III measurements of NO_3 is the primary objective of this task, every effort will be made to obtain accurate ground track and occultation timing from the SAGE III team to coordinate the satellite and ground-based measurements. Because of the spatial and temporal variability of NO_3, the comparisons between satellite and ground-based measurements must be made carefully. The number of validation opportunities will increase significantly if the spectrograph becomes portable, so every effort will be made to acquire this capability before launch.

Exchange of Correlative Data with Instrument Team and Other Investigators: It is our intention to disseminate the correlative data from this investigation to the Instrument Team as quickly as possible. Data from the correlative measurements will be available on our ftp site for rapid dissemination to interested users.

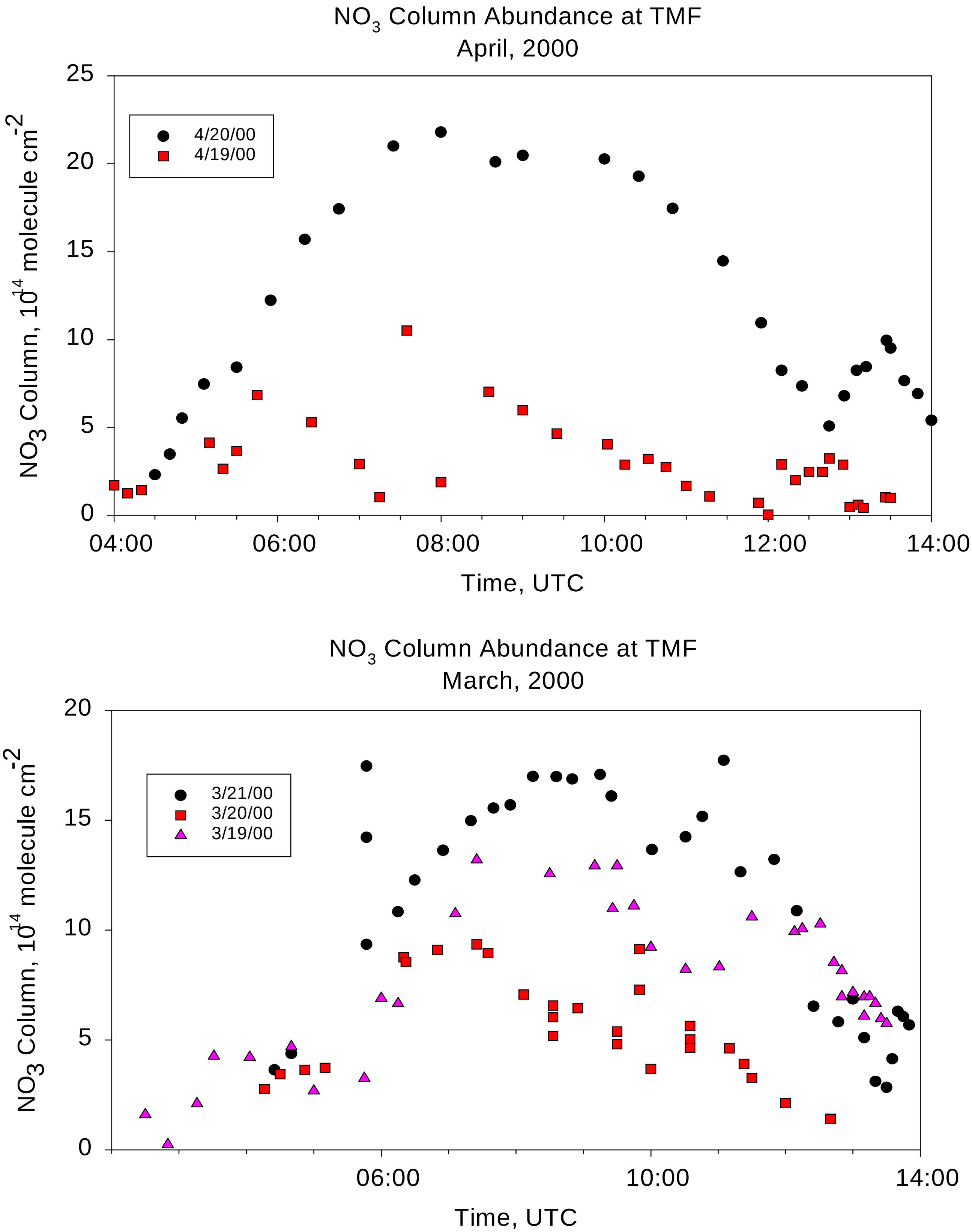

Figure 1. Diurnal NO_3 vertical column abundance measurements from TMF for the months of March (lower panel) and April 2000. Spectra were collected and analyzed by V. Nemtchinov.